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Structure of *catena*-Aqua(2,2′-bipyridine)(2-imidazolidinethione-*S*)-μ-[sulfato(2–)-*O*:*O*′]-cadmium(II) Monohydrate and its Solid-State ^{113}Cd NMR Spectrum

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Abstract. [Cd(SO$_4$)(C$_3$H$_6$N$_2$S)(C$_{10}$H$_8$N$_2$)(H$_2$O)].H$_2$O, $M_r = 502\cdot84$, monoclinic, $P2_1/n$, $a = 6\cdot736$ (1), $b = 25\cdot728$ (3), $c = 10\cdot011$ (2) Å, $\beta = 90\cdot72$ (2)°, $V = 1734$ (1) Å^3, $Z = 4$, $D_m = 1\cdot91$ (2), $D_x = 1\cdot93$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 15\cdot2$ cm^{-1}, $F(000) = 1008$, $T \simeq 298$ K, $R(F) = 0\cdot044$ for 3285 reflections. The structure may be described as six-coordinate Cd$^{\rm II}$ species which are bridged by two different O atoms of sulfate ions to form an infinite chain of the type: –OSO$_2$O–Cd–OSO$_2$O–. The remaining intermolecular distances are normal van der Waals distances. The coordination polyhedron of Cd$^{\rm II}$ may be described in terms of an approximate octahedron with a water O atom, an S atom and two N atoms from the bipyridine in the equatorial plane and sulfate O atoms in the axial positions. The water of hydration is hydrogen bonded to the coordinated water. The Cd–O(SO$_4$) distances are 2·273 (4) and 2·298 (4) Å, whereas the Cd–O(H$_2$O) distance is 2·315 (4) Å. The Cd–S and Cd–N distances are 2·628 (1) and 2·373 (5), 2·393 (5) Å, respectively. The cross-polarization magic-angle spinning ^{113}Cd NMR signal is observed at 137 p.p.m., deshielded relative to the solid Cd(ClO$_4$)$_2$ in Al$_2$O$_3$ standard. The principal components of the chemical shift tensor were calculated from the spinning side bands and were found to be +285, +137 and –10 p.p.m. No solution ^{113}Cd NMR was observed.

Introduction. In recent years there has been considerable research effort expended in the application of ^{113}Cd NMR to the solution of problems dealing with metal sites in a wide variety of chemical and biological compounds (Rodesiler, Turner, Charles, Griffith & Amma, 1984; Armitage & Boulanger, 1983; Ellis, 1983). The development of solid-state cross-polarization magic-angle spinning (CP/MAS) ^{113}Cd NMR has even further enhanced the potential utility of this metal-ion probe (Ackermann, Orr, Bartuska & Maciel, 1979; Mennitt, Shatlock, Bartuska & Maciel, 1981; Maciel, 1984; Marchetti, Ellis & Bryant, 1985). The combination of X-ray crystallography and (CP/MAS) NMR offers an excellent opportunity to study and attempt to correlate metal-ion geometry with ^{113}Cd NMR chemical shifts, and perhaps by this means to convert ^{113}Cd NMR into a much more useful chemical tool. The ultimate goal of such studies is to be

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able to observe the ^{113}Cd NMR signal in the solid or in solution and to be able to describe the ligands and the stereochemistry of these ligands about the Cd atom or the stereochemistry of a metal ion which has been substituted by Cd. To this end we have been actively synthesizing compounds, determining their crystal structures, measuring the CP/MAS ^{113}Cd NMR and the solution ^{113}Cd NMR as well. We report here a portion of this on-going research program.

Experimental. A solution containing 1·56 g (0·01 mol) 2,2′-bipyridine (Columbia Organic) was added slowly with stirring to a solution of 2·59 g (0·003 mol) $3CdSO_4.8H_2O$ (MCB) and 1·76 g (0·02 mol) 2-imidazolidinethione (Columbia Organic). The total volume of approximately 150 ml was heated gently (333 K) for 15 min, then allowed to evaporate at ambient temperature. Diffraction quality crystals were collected by gravity filtration after one week and either sealed in thin-walled capillaries for X-ray diffraction studies or stored for NMR measurements. Enraf–Nonius CAD-4 diffractometer interfaced to PDP 11/60, crystal aligned and intensity data collected by standard techniques (Enraf–Nonius, 1982). D_m by flotation in $CCl_4/HCBr_3$ mixtures. $h0l$, $h+l=2n+1$; $0k0$, $k=2n+1$ absent; crystal 0·22 × 0·11 × 0·62 mm; faces: (010), (0$\bar{1}$0), (100), ($\bar{1}$00), (102), ($\bar{1}$02), (10$\bar{2}$), ($\bar{1}$0$\bar{2}$); numerical absorption correction (based on Gaussian integration formula), max., min. transmission factors 0·846–0·716; graphite monochromator, $\theta = 6\cdot1°$; $P = 0\cdot030$ in $\sigma(F_o^2) = [\sigma(I_{\rm raw})^2 + (PI_{\rm raw})^2]^{1/2}/{\rm Lp}$; data considered non-zero if F^2 greater than $4\sigma(F^2)$, 4377 independent hkl's measured in ω–2θ mode to $2\theta_{\max} = 57°$, $(\sin\theta)/\lambda = 0\cdot6714$ Å^{-1}, hkl range 0 to 9, 0 to 34, −13 to 13; 3285 reflections used; variable scan speed of 0·7–3·3° min^{-1} with preliminary scan speed of 3·3° min^{-1} 2θ, scan parameter, DOMA, = 0·650; 25 general reflections used to determine orientation matrix (checked fully every 24 h) and used for all parameter measurements in 2θ range = 22–35°; intensity and orientation of three standard reflections (382, 3,11,$\bar{2}$, $\bar{2}\bar{7}\bar{7}$) monitored every 2 h, with overall decay less than 1%I; structure solved by standard heavy-atom methods and refined by full-matrix least squares, anisotropic temperature factors and anomalous-dispersion corrections with weights based upon intensity statistics; function minimized $\sum_i w_i[|F_o|_i - |F_c|_i]^2$ where $w = 1/[\sigma(F_o)]^2$; final least squares performed with f, f' and f'' from *International Tables for X-ray Crystallography* (1974); largest shift at end of refinement $= 0\cdot02\sigma$, $a\delta = 0\cdot01\sigma$, No. of variables 235; final $R = 0\cdot044$, $wR = 0\cdot061$; e.s.d. of observation of unit weight = 2·67; H atoms were located from difference Fourier maps but neither coordinates nor temperature factors were refined; the highest peak on the final difference map was 2·1 e Å^{-3} and the lowest peak −1·6 e Å^{-3}, both of which were within 1 Å of the Cd atom; all computer programs used were either those in the Enraf–Nonius *SDP* package (Frenz, 1982) on the PDP 11/60 or the Microvax II. *ORTEP*II (Johnson, 1971) calculated on an IBM 3081. The atomic coordinate parameters and errors are listed in Table 1.* Selected interatomic distances and angles and e.s.d.'s are listed in Table 2. The experimental conditions and equipment for the ^{113}Cd NMR have been described elsewhere (Charles, Griffith, Rodesiler & Amma, 1983). The principle components of the ^{113}Cd shielding tensor were determined by Simplex optimization of computed spinning sideband intensities to the experimental values

Table 1. *Positional parameters and their e.s.d.'s*

Anisotropically refined atoms are given in the form of an isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

	x	y	z	B(Å^2)
Cd	0·09852 (5)	0·86687 (1)	0·19419 (3)	1·647 (6)
S(1)	0·1994 (2)	0·89470 (7)	0·4383 (1)	2·70 (3)
S(2)	0·6004 (2)	0·90300 (5)	0·1563 (1)	1·72 (2)
O(1)	0·4266 (6)	0·8686 (2)	0·1441 (5)	3·09 (8)
O(2)	−0·2383 (6)	0·8735 (2)	0·2237 (4)	3·08 (9)
O(3)	0·5561 (7)	0·9484 (2)	0·2368 (4)	3·13 (9)
O(4)	0·6645 (6)	0·9179 (2)	0·0210 (4)	2·60 (8)
O(5)	0·0587 (6)	0·9429 (2)	0·0729 (4)	2·42 (7)
O(6)	0·1627 (6)	0·4563 (2)	0·6344 (4)	2·93 (8)
N(1)	0·0897 (6)	0·7766 (2)	0·2422 (5)	2·05 (8)
N(2)	0·0721 (7)	0·8168 (2)	−0·0066 (5)	2·18 (8)
N(3)	−0·1800 (7)	0·9244 (2)	0·4859 (5)	3·1 (1)
N(4)	0·0313 (8)	0·9436 (2)	0·6455 (5)	2·9 (1)
C(1)	0·0082 (9)	0·9221 (2)	0·5231 (5)	2·1 (1)
C(2)	−0·2972 (9)	0·9560 (3)	0·5801 (6)	3·1 (1)
C(3)	−0·157 (1)	0·9624 (3)	0·6961 (6)	3·2 (1)
C(4)	0·0784 (8)	0·7431 (2)	0·1402 (6)	2·03 (9)
C(5)	0·064 (1)	0·6898 (2)	0·1641 (7)	3·1 (1)
C(6)	0·064 (1)	0·6712 (3)	0·2901 (8)	3·9 (1)
C(7)	0·074 (1)	0·7067 (3)	0·3970 (6)	3·3 (1)
C(8)	0·0852 (9)	0·7583 (2)	0·3679 (5)	2·6 (1)
C(9)	0·0782 (7)	0·7647 (2)	0·0031 (5)	1·99 (9)
C(10)	0·0829 (9)	0·7336 (2)	−0·1086 (6)	2·8 (1)
C(11)	0·080 (1)	0·7559 (3)	−0·2335 (6)	3·4 (1)
C(12)	0·072 (1)	0·8091 (3)	−0·2446 (6)	3·6 (1)
C(13)	0·072 (1)	0·8380 (2)	−0·1280 (6)	3·0 (1)

Table 2. *Selected bond distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

Cd–S(1)	2·628 (1)	Cd–O(5)	2·315 (4)
Cd–O(1)	2·273 (4)	Cd–N(1)	2·373 (5)
Cd–O(2)	2·298 (4)	Cd–N(2)	2·393 (5)
		O(5)–O(6)	2·836 (4)

S(1)–Cd–O(1)	87·7 (1)	O(1)–Cd–N(2)	83·5 (2)
S(1)–Cd–O(2)	96·0 (1)	O(2)–Cd–O(5)	84·1 (1)
S(1)–Cd–O(5)	106·5 (2)	O(2)–Cd–N(1)	91·2 (2)
S(1)–Cd–N(1)	94·9 (1)	O(2)–Cd–N(2)	94·9 (2)
S(1)–Cd–N(2)	160·8 (1)	O(5)–Cd–N(1)	158·4 (1)
O(1)–Cd–O(2)	172·4 (2)	O(5)–Cd–N(2)	90·5 (1)
O(1)–Cd–O(5)	88·5 (1)	N(1)–Cd–N(2)	69·0 (2)
O(1)–Cd–N(1)	95·2 (2)	Cd–S(1)–C(1)	112·8 (2)
		Cd–O(5)–O(6)	114·4 (5)

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, all intramolecular distances and angles, and details of least-squares planes as well as the observed and simulated ^{113}Cd NMR spectra have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43736 (59 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

(Maricq & Waugh, 1979; Herzfeld & Burger, 1980; Box, Hunter & Hunter, 1978) and a good fit was obtained. The optimization procedure involved a two parameter fit which resulted in best estimates for the anisotropy, δ, and the asymmetry parameter, η. These two parameters along with the rotor spinning speed and the spectrometer frequency determine the relative sideband intensities in the MAS spectra. From these optimized parameters the best estimates of the principle values of the Cd shielding tensor were obtained. The calculation was carried out on a VAX 780 with a program written by P. Marchetti (Marchetti, Ellis & Bryant, 1985). For this case: $\eta = 0{\cdot}9967$, $\delta = 222$ p.p.m.

Discussion. The crystal structure of the title compound may be described as a chain structure in which the six-coordinate Cd^{II} ions are linked to each other *via* two different O atoms of a sulfate ion in such a manner that the O atoms of the bridging sulfate groups are in a *trans* position of the Cd^{II} central ion, Fig 1. The intermolecular distances are normal van der Waals distances and there is a normal hydrogen-bonded distance [O(6)—H(5*B*), 1·87 Å] involving the water molecule of hydration not bound to the metal and the H of the water in the coordination sphere. The coordination polyhedron of Cd^{II} is made up of two N atoms from the chelating bipyridine moiety, an S atom from the imidazolidinethione ligand, an O atom from a water molecule (all in an approximate equatorial plane) and O atoms in the *trans* position from bridging sulfate groups, Fig. 2. The Cd—S distance of 2·628(1) Å is, as expected, longer than the sum of the covalent radii (2·52 Å) but shorter than that found for a mercaptide complex, 2·715 (3) Å (Griffith, Rodesiler & Amma, 1985). The C(1)—S(1)—Cd angle of 112·8 (2)° is consistent with the use of an sp^3 hybridized S orbital in bonding to the metal. This bonding mode for thiourea complexes has been previously observed by us (Berta, Spofford, Boldrini & Amma, 1970, and references therein) and others. The Cd—O distances are essentially the same value for all three, but Cd—O(sulfate) is surprisingly short considering the poor donor ability of the sulfate ion. The remaining intramolecular distances and angles are normal.

The sum of the bond angles around Cd involving N(1), N(2), S(1) and O(5) (360·8°) and the least-squares plane including these atoms as well as the Cd atom shows these atoms to form an approximate plane, $\sim\pm 0{\cdot}1$ Å (the equatorial plane). This plane is distorted by S(1) and N(2) toward O(1) by approximately 0·1 Å and O(5) and N(1) toward O(2) by approximately 0·1 Å. The O(2)—Cd—O(1) angle is somewhat distorted from the ideal linear value at 172·4 (2)°.

The solid-state CP/MAS ^{113}Cd NMR shows a single peak at 137 p.p.m., deshielded relative to the $Cd(ClO_4)_2.6H_2O$ dispersed in Al_2O_3. No solution ^{113}Cd NMR could be obtained because either the compound was insoluble or decomposed in solvents suitable for NMR experiments. The 137 p.p.m. value is to be compared with the value of 25 p.p.m. found in diaquabis(benzoato)cadmium(II) compounds (Rodesiler, Griffith, Charles & Amma, 1985). This difference reflects the strong deshielding effect of the one S atom in the coordination sphere but opposed by the strong shielding effect of the sulfate O atoms. These

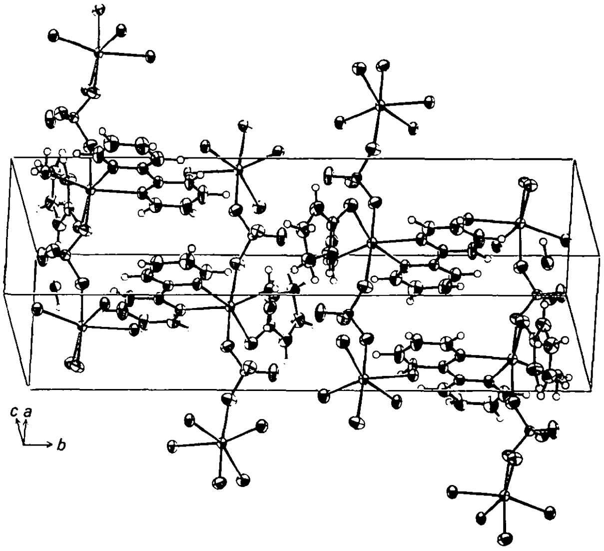

Fig. 1. *ORTEP*II (Johnson, 1971) drawing of the contents of the unit cell. The thermal ellipses are drawn at the 50% probability level. The H atoms are drawn with an arbitrary radius of 0·1 Å and are represented by open circles.

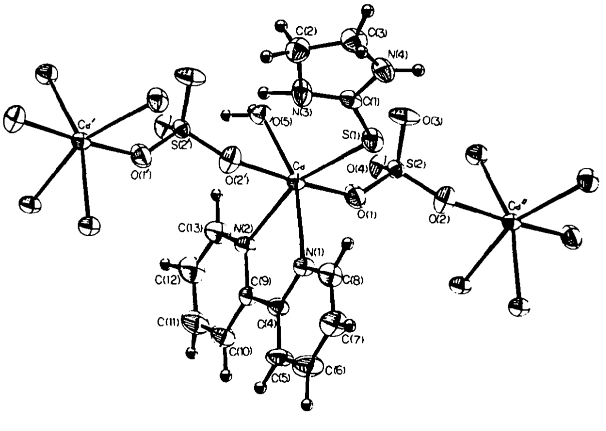

Fig. 2. *ORTEP*II (Johnson, 1971) drawing of the local environment about the Cd atom. The coordination polyhedron is readily seen. The thermal ellipsoids are drawn at the 50% probability level and the H atoms are drawn with an arbitrary 0·1 Å radius. The primed atoms are related by translation along **a**, as are the double primed atoms.

opposing effects on the ^{113}Cd shielding tensor are shown by the principal components of +285, +137 and −10 p.p.m. In the absence of single-crystal ^{113}Cd NMR data we cannot know with certainty the direction of these components but the crystal structure permits us to make some reasonable guesses. A thiourea S might contribute +300 p.p.m., a water O atom 0 p.p.m., a bipyridine N +9 p.p.m. and a sulfate O −100 p.p.m. (Honkonen, Marchetti & Ellis, 1986). A component of the chemical shift tensor reflects the contribution to the chemical shift of chemical species in the plane normal to this component. Therefore, the direction of the +285 component should be parallel to or make only a small angle with the O—Cd—O line. The other two components are more difficult to locate with the meagre information presently available but they must be approximately in the CdN_2OS plane. Hopefully, in the future as more of the present type of data become available, more specific interpretations of the chemical shift tensor can be made.

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Structure of (2,4-Dinitrophenolato)(triethanolamine)lithium Monohydrate*

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Abstract. $[Li(C_6H_3N_2O_5)\{N(CH_2CH_2OH)_3\}].H_2O$, M_r = 357·2, monoclinic, $C2/c$, $a = 25{\cdot}731\,(5)$, $b = 6{\cdot}426\,(4)$, $c = 21{\cdot}831\,(5)$ Å, $\beta = 112{\cdot}81\,(4)°$, $V = 3327{\cdot}40$ Å^3, $Z = 8$, $D_x = 1{\cdot}426$, D_m (by flotation) $= 1{\cdot}372$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 1{\cdot}22$ cm^{-1}, $F(000) = 1504$, room temperature, $R = 0{\cdot}053$ for 1273 observed reflections. Lithium is five-coordinated to the four heteroatoms of triethanolamine

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* Triethanolamine is 2,2′,2″-nitrilotriethanol.

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